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(54) Title: GLASSES CONTAINING RARE EARTH FLUORIDES

(57) Abstract

This process provides a new way to embed rare earth fluorides into silica (or germania–doped silica) glasses by solution chemistry. Embedding rare earth fluorides into a silica (or germania–doped silica) glasses comprises the following steps. The first step forms a porous silica core preform by OVD process. The second step submerges the preform into an aqueous solution of rare earth ions. The third step removes the preform from the solution and washes the outside surfaces of the preform. The fourth step submerges the preform into an aqueous solution of a fluorinating agent, such as ammonium bifluoride, HF or KF. Rare earth trifluorides precipitate out from the solution and deposit on the wall of pores. This is followed by drying.

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GLASSES CONTAINING RARE EARTH FLUORIDES

TECHNICAL FIELD

This invention relates to a new process for embedding rare earth fluorides into silica glasses. The new embedded glasses are useful as optical amplifiers for telecommunications.

BACKGROUND ART

All optical amplifiers, and particularly erbium doped fiber amplifiers have experienced explosive deployment in fiber optic telecommunication systems because of the well-recognized advantages that these types of devices have over repeater type amplification schemes. For example, the erbium doped fiber amplifier (EDFA) conveniently operates in the preferred 1550 nm third telecommunications spectral window, has high polarization-insensitive gain, low cross talk between signals at different wavelengths, good saturation output power, and a noise figure close to the fundamental quantum limit. The excellent noise characteristics potentially allow hundreds of amplifiers to be incorporated along the length of a fiber telecommunications link which could then span thousands of kilometers. Optical amplifiers, and particularly EDFAs in contrast to electronic repeaters, are also transparent to data rate, signal format and wavelength over a limited range, making them especially useful for wavelength multiplexed communication systems that simultaneously transmit a large number of signals using different wavelength bands for each signal.

Currently, germania-doped silica and heavy metal fluoride (such as ZBLAN) glasses are used as hosts for rare earth ions, such as Erbium and praseodymium, to make fiber amplifiers. Silica base glasses are chemically and mechanically stable. They easily are fabricated and fused into the

germania-doped silica communication fibers. However, silica glasses are inefficient for infrared upconversion because of their large phonon energy. On the other hand, fluoride glasses have low phonon energy, but are very difficult to fiberize. They are also hard to fuse with the silica fibers.

Transparent oxyfluoride glass-ceramics which are comprised of fluoride microcrystals in the mainly oxide glass matrices offer unique properties of high chemical durability of oxide glasses and low phonon energy environment for the rare earth ions of fluoride glasses or crystals. These glass-ceramics are made by melting oxides and fluorides of the cation components to form oxyfluoride glasses. Heat treatment then precipitates out fluoride micro-crystals (ceramming). Because these transparent oxyfluoride glass-ceramics generally have lower melting temperatures, higher refractive indexes and higher thermal expansion coefficients than silica glasses, they may pose a challenge to making fiber amplifiers with pure silica overcladding.

Accordingly, there continues to be a need for CTE-matched optical amplifiers and methods for making such products. In particular, there is a need for new ways for embedding rare earth fluorides into glasses suitable for making optical amplifiers.

DISCLOSURE OF THE INVENTION

Briefly, the present invention relates to a silica-based glass containing rare earth fluoride crystals. In another aspect, the invention relates to a method for embedding rare earth fluorides into silica-based (or germania-doped silica) glasses by solution chemistry. By silica-based I mean glass having silica and/or germania-doped silica as the predominant component.

The rare earth fluoride doped silica preforms of this invention comprise:

Component	Weight Percent
SiO_2 and GeO_2	85-99.0
Al_2O_3 and Ga_2O_3	0-14.9
Re_xF_y	0.01-2.0
R_xFy	0.1-2.0

wherein X and Y are integers. The sums such as SiO_2 + GeO_2 are fully interchangeable. Each component could range from 0-99% as long as the total SiO_2 + GeO_2 is between 85 and 99%. The sums of Al_2O_3 and Ga_2O_3 also are interchangeable. R is alkali or alkaline-earth ions such as Na, K, Li, Ca and Mg.

BEST MODE OF CARRYING OUT INVENTION

As contemplated herein, embedding rare earth fluorides into a silica (or germania-doped silica) glasses comprises the following steps. The first step forms a porous silica core preform by OVD process. Preferably, the preform has a pore size of about 500 nm or less, more preferably, in the range of 200 to 500 nm. The second step submerges the preform into an aqueous solution of rare earth ions. Preferably the solution is a nitrate solution such as $Er(N03)_3$, $Pr(N03)_3$, $Nd(NO_3)_3$, $Dy(N0_3)_3$, or a combination of these nitrates. At this stage, the pores in the preform fill with the aqueous solution of rare earth ions. The third step removes the preform from the nitrate solution and washes out the extra amount of nitrate on the outside surfaces of the preform using deionized water. The fourth step submerges the preform into an aqueous solution of a fluorinating agent, such as ammonium bifluoride, ammonium fluoride, HF or KF. F ions diffuse into the pores and the following reaction occurs,

$$Re^{=3} + 3F- \quad ReF_3$$

Rare earth trifluorides precipitate out from the solution and deposit on the wall of pores.

The fifth step dries the preform at about 300 C in a vacuum to remove the remaining water inside the pores. Generally, after the drying step the preform is still porous.

The sixth step heats the preform again in a chlorine or fluorine environment to remove any residual water and finally consolidates the preform into a non-porous glass body which may serve as a preforms for other useful articles and devices such as fibers for optical amplifiers.

The melting points of rare earth fluorides range from 1143 C(HoF_3) to 1515 C (ScF_3), which are lower than the melting point of silica (1710 C) and close to the sintering temperature of germania-doped silica. Therefore, in the sixth step, normal consolidation procedure for OVD core preforms can be used to consolidate the fluoride-silica preforms.

In another embodiment, the fourth step may be carried out by flowing/diffusing fluorine or fluorine-containing gases such as HF into the pores of the preform.

The refractive indexes of the embedded fluorides can be adjusted by mixing the rare earth fluorides with alkali or alkaline earth fluorides, such as LiF (n_D = 1.395), CaF_2 (n_D - 1.434), SrF (n_D = 1.442) and MgF_2, which have lower refractive indexes and low solubilities in water. The size of fluoride

microcrystals can be adjusted by controlling the concentration of solutions and pore surface treatments.

Doping the glasses with a rare earth metal is desirable for enhancing the emission and absorption spectra, as discussed above. Therefore, the silica preforms of the present invention include a rare earth element, such as Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu. Preferably, the rare earth element is Er, Pr, Eu or Dy. Even more preferably, the rare earth element is Er (e.g., ErF_3). The glasses also may contain various other components. For example, the glasses may further include up to 5 wt.% of other oxides, such as Y_2O_3, La_2O_3, CdO, B_2O_3, SnO, ZrO_2, P_2O_5, Sb_2O_5, As_2C_5 or Bi_2O_3.

The rare earth fluoride-containing, silica-based glass of the invention is suitable for making fibers for optical amplifiers which offer the unique properties of transparent oxyfluoride glass-ceramics discussed above. In addition, the inventive silica-based optical amplifiers, when used with silica overcladding, provide the added benefit of matched CTE and refractive index between the fiber and the cladding.

In addition to these embodiments, persons skilled in the art can see that numerous modifications and changes may be made to the above invention without departing from the intended spirit and scope thereof.

I CLAIM:

1. A process for embedding rare earth fluorides into silica glasses comprising the steps of:

providing a porous silica preform;

submerging the preform into an aqueous solution of rare earth ions;

removing the preform from the aqueous solution of rare earth irons;

washing the preform removed from the aqueous solution of rare earthed ions;

submerging the washed preform into an aqueous solution of a fluorinating agent, thereby precipitating rare earth trifluorides onto the preform; and

drying the preform.

2. A process according to claim 1 including the additional step of drying the dried preform again in a chlorine or fluorine environment.

3. A process according to claim 1 wherein the porous silica preform is made by oxide vapor deposition.

4. A process according to claim 1 wherein the porous silica preform has a pore size of about 500 nm.

5. A process according to claim 1 wherein the aqueous solution of rare earth ions is a nitrite solution of $Er(N03)_3$, $Pr(N0_3)_3$, $Nd(N0_3)_3$, $Dy(N03)_3$ and combinations thereof.

6. A process according to claim 1 wherein the washing of the preform removed from the aqueous solution of rare earth ions is carried out using deionized water.

7. A process according to claim 1 wherein the fluorinating agent is ammonium fluoride, ammonium bifluoride, HF or KF.

8. A process according to claim 1 wherein the aqueous solution of rare earth ions fills the pores of the porous silica preform.

9. A process according to claim 1 wherein the fluorinating agent fuses into the pores of the porous silica preform and react with the rare earth ions.

10. A process according to claim 9 wherein the reaction produces rare earth trifluorides.

11. A process according to claim 1 wherein the preform is dried at about 300 C in a vacuum.

12. A process according to claim 1 wherein the silica is a germania-doped silica.

13. A process according to claim 1 further comprising the step of consolidating the preform to form a non-porous structure.

14. A porous silica preform having a pore size of about 500 nm embedded with rare earth fluorides.

15. A preform according to claim 14 wherein the silica is germania-doped silica.

16. A preform according to claim 14 wherein the rare earth fluorides are rare earth trifluorides.

17. A preform according to claim 14 wherein the rare earth ions are Er, Pr or Ty.

18. A preform according to claim 14 having a composition of:

Component	Weight Percent
SiO_2 and GeO_2	85-99

Al_2O_3 and Ga_2O_3	0-14.9
Re_xF_y	0.01-2.0
R_xFy	0.1-2.0

wherein X and Y are integers; R is alkali or alkaline earth ions.

19. A preform according to claim 18 wherein Re is Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

20. A preform according to claim 18 wherein Re is Er, Pr, Nd, Eu or Dy.

21. A preform according to claim 18 wherein Re_xF_y is ErF_3.

22. A preform according to claim 14 including 0-5 wt.% of Y_2O_3, La_2O_3, CdO, B_2O_3, SnO, ZrO_2, P_2O_5, Sb_2O_5, As_2C_5 or Bi_2O_3.

23. A fiber suitable for use as an optical fiber amplifier made from the preform of claim 14.

24. A non-porous fiber preform comprising silica-based glass characterized in that said glass has embedded therein, rare earth fluoride crystals.

25. A fiber suitable for use in an optical amplifier comprising the non-porous fiber preform according to claim 24.

27. An optical amplifying device comprising the glass fiber of claim 22.

28. An electrical optical device made from the preform of claim 14.

29. Silica-based glass containing rare earth fluoride crystals.

30. Optical fiber comprising the silica-based glass according to claim 29.

31. Optical amplifier comprising the optical fiber according to claim 30.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/06130

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G02B 6/13
US CL : 385/141, 65/385

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 385/141-145, 65/385, 426, 444, 446

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST
search terms: fluoride, halide, halogen, rare earth, silicate, silica, sio2, geo2, trifluoride, glass

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ------ X	US 5,262,365 A (OYOBE ET AL) 16 NOVEMBER 1993 (16/11/1993), SEE ENTIRE DOCUMENT.	16-23 -------- 24-31
X ----- Y	US 4,263,031 A (SCHULTZ) 21 APRIL 1981 (21/04/1981), SEE ENTIRE DOCUMENT.	14-15 -------- 16-23
A	US 4,936,650 A (AINSLIE ET AL) 26 JUNE 1990 (26/06/1990), SEE ENTIRE DOCUMENT.	1-31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

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24 APRIL 2000	03 MAY 2000
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INTERNATIONAL SEARCH REPORT

Intea. ional application No.
PCT/US00/06130

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Inter..ional application No.
PCT/US00/06130

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)1-13, drawn to a process of making a silicate optical glass.
Group II, claim(s) 14-31, drawn to a composition of a silicate optical glass, and an optical fiber and an optical amplif ier made of that glass.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the composition of a silicate optical glass of claims in Group II do not require any special techinical features of the process of the making such as a solution doping method of claims in Group I.